# Vibrational spectra of (=O → Si)-(aroyloxymethyl)trifluorosilanes

G.A. Gavrilova *, N.N. Chipanina, Yu.L. Frolov, L.I. Gubanova
and M.G. Voronkov

*Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, 664033 Irkutsk (USSR)*

(Received March 14th, 1991)

**Abstract**

The IR spectra of (aroyloxymethyl)trifluorosilanes $4\text{-}X\text{-}C_6H_4COOCH_2SiF_3$ (AFS) containing an intramolecular O → Si coordinate bond, have been examined in the 500–200 $cm^{-1}$ region. The band near 330 $cm^{-1}$ is assigned to the O → Si bond stretching vibration because of its λ sensitivity to changes in the polarity of the medium and because of its response to the nature of substituent X as well as to the formation of AFS-pyridine complexes.

Normal-coordinate analysis of a model compound $HCOOCH_2SiF_3$ has been carried out. By use of a set of frequency partial derivatives by force constants a force field corresponding to the experimental frequencies and equilibrium geometry of $4\text{-}F\text{-}C_6H_4COOCH_2SiF_3$ has been selected. The $\nu(O \to Si)$ stretching vibration is delocalized by three low-frequency motions 360, 330 and 218 $cm^{-1}$. The effect of electronic and kinematic factors on the AFS vibrational spectra has been evaluated.

## Introduction

The presence of intramolecular coordinate O → Si bond in (aroyloxymethyl)trifluorosilanes, $4\text{-}X\text{-}CH_6H_4COOCH_2SiF_3$ (X = $OCH_3$, $CH_3$, H, F, Cl, Br, $NO_2$) in the crystalline and gaseous states, as well as in solutions, has been established by X-ray diffraction, NMR and IR spectroscopy and by dielectrometry [1–3]. The O → Si bond strength has been shown to depend on the electron effect of the substituent X and the parameters $\epsilon$ and $n$ of the medium. The IR spectra of AFS were examined in the gaseous and the solid states and in organic solvents in the 4000–400 $cm^{-1}$ region [4,5]. This enabled the main responses of the $\nu(C=O)$, $\nu(C-O-C)$, $\nu(SiF_{ax})$, and $\nu(SiF_{eq})$ frequencies upon changing the O → Si bond strength to be established. With increasing the donating properties of the substituent X and the polarity of the medium, the $\nu(C=O)$ and $\nu(SiF)$ frequencies are reduced whereas those of $\nu(C-O-C)$ are increased which indicates strengthening of the intramolecular coordinate O → Si bond. The enthalpy ($\Delta H$) of intramolecular coordination of the silicon atom in compounds of the series $C_6H_5COO\text{-}CH_2SiF_n(CH_3)_{3-n}$ grows in step with the number of fluorine atoms ($n$) in the following sequence:

| | $n = 1$ | $n = 2$ | $n = 3$ |
|---|---|---|---|
| $\Delta H$ | 5.4 | 11.7 | 33 kJ/mol |

In order to distinguish the absorption bands caused by participation of the O → Si bond in stretching and skeletal vibrations, we have examined low-frequency IR spectra in the 500–200 cm$^{-1}$ region. A tentative assignment of the IR absorption bands in the 4000–200 cm$^{-1}$ region has been made. On this basis a harmonic approximation has been suggested.

*The intramolecular coordinate O → Si bond vibration in the IR spectra of (aroyloxy-methyl)trifluorosilanes*

Calculations of normal vibrations for the well-known intracomplex pentacoordinate silicon compound, 1-hydrosilatrane, [6] has shown the existence of two low-frequency vibrations which depend on the coordinate N → Si interaction. The 586 and 446 cm$^{-1}$ bands in the vibrational spectrum have been assigned to these vibrations. For hexacoordinate silicon compounds $SiF_4 \cdot 2L$ [7] with different nitrogen-containing ligands (L), the bands in the 380–440 cm$^{-1}$ region have been assigned to the $\nu(N \rightarrow Si)$ vibrations. If the O → Si bond in AFS is weaker than the N → Si bond in silatranes, the $\nu(O \rightarrow Si)$ band would be expected in the 400–200 cm$^{-1}$ region. As with silatrane molecules, the coordinate O → Si bond vibration does not seem to be localized at a certain band, on the contrary, it is most likely to be spread over some low-frequency vibrations of the molecule.

The IR spectra in the 500–200 cm$^{-1}$ region were obtained for AFS solutions in different organic solvents (n-$C_6H_{12}$, $CCl_4$, $(C_4H_9)_2O$, $ClCH_2$–$CH_2Cl$, $CH_3CN$, $C_5H_5N$, $C_5D_5N$) and for the solid state (in Nujol). The IR spectra of AFS solutions in organic solvents in the 4000–400 cm$^{-1}$ region imply that the bands of the stretching vibrations arising from C=O, Si–$F_{ax}$, and C–O–C groups attached to the O → Si bond, are very sensitive to polarity of the medium. The vibration frequencies of these groups obey the Buckingham equations [4] with X = F:

$$\nu(C{=}O) = 1692 - 91(\epsilon - 1)/(2\epsilon + 1) - 38(n^2 - 1)/(2n^2 + 1) \qquad R = 0.995$$

$$\nu(Si{-}F_{ax}) = 834 - 108(\epsilon - 1)/(2\epsilon + 1) - 18(n^2 - 1)/(2n^2 + 1) \qquad R = 0.999$$

$$\nu(C{-}O{-}C) = 1351 + 37(\epsilon - 1)/(2\epsilon + 1) - 13(n^2 - 1)/(2n^2 + 1) \qquad R = 0.975$$

In this case the dipole–dipole interaction is preferable. With increasing polarity of the medium a low-frequency shift of the $\nu(C{=}O)$ and $\nu(Si{-}F_{ax})$ bands and a high-frequency shift of the $\nu(C{-}O{-}C)$ band are observed which suggest increasing strength of the intramolecular coordinate O → Si bond. Consequently, with increasing $\epsilon$ value of the solvent, the $\nu(O \rightarrow Si)$ value might be expected to increase. Of all the frequencies in the 400–200 cm$^{-1}$ region, the band at $\sim 330$ cm$^{-1}$ present in all the AFS spectra proved to be most sensitive to the change in $\epsilon$ (Figs. 1 and 2). It is likely to be one of the bands corresponding to the $\nu(O \rightarrow Si)$ stretching vibration. Figure 3 shows a dependence of the band frequency in the IR spectra of 4-F-$C_6H_4COOCH_2SiF_3$ (I) upon polarity of the medium. The equation describing this dependence is as follows:

$$\nu(O \rightarrow Si) = (321 \pm 2) + (36 \pm 7)(\epsilon - 1)/(2\epsilon + 1) \qquad R = 0.904$$

The free member value in this linear equation corresponds to the $\nu(O \rightarrow Si)$ value for I in the gaseous state (with $\epsilon = 1$).

The AFS high-frequency spectra show that substituent X in the benzene ring *para*-position (X = $OCH_3$, $CH_3$, H, F, Cl, Br, $NO_2$) influences the strength of the
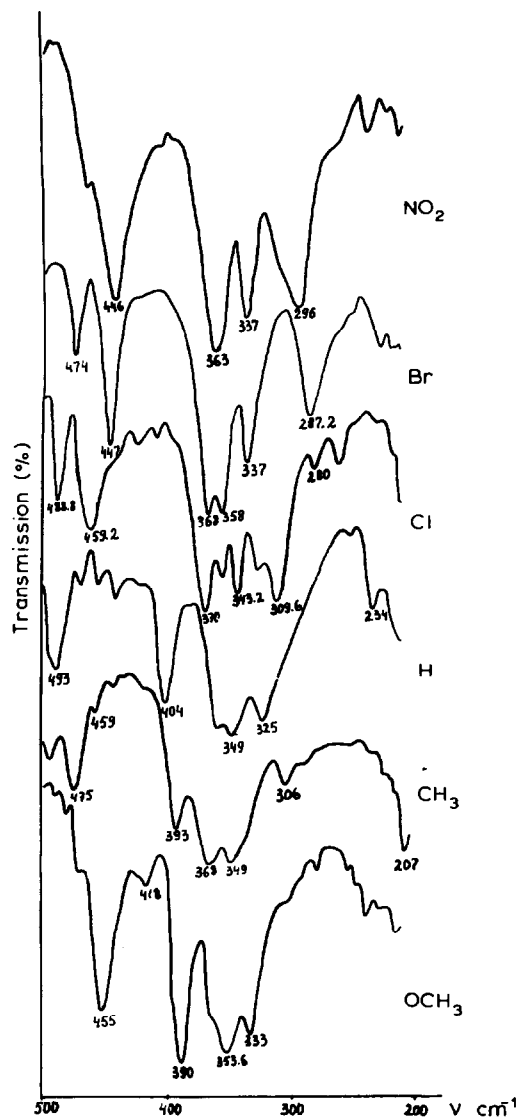
Fig. 1. IR spectra of AFS in the 500–200 cm$^{-1}$ region (Nujol).

intramolecular O → Si bond [5]. An increase in the donor properties of the sub-stituent X increases the strength of coordination. In this case the $\nu$(C=O) and $\nu$(Si–F$_{ax}$) frequencies are reduced whereas the $\nu$(C–O–C) frequency is enhanced. These frequency values in the spectra of AFS in both the solutions and the solid state meet the Hammett equations. Thus for AFS solutions in CCl$_4$ the following equations are effective:

$$\nu(\text{C=O}) = 1658 + (31 \pm 1.8)\sigma_n \qquad R = 0.988$$
$$\nu(\text{C–O–C}) = 1358 - (12 \pm 1.7)\sigma_n \qquad R = 0.944$$
$$\nu(\text{Si–F}_{ax}) = 813 + (20 \pm 2)\sigma_n \qquad R = 0.967$$
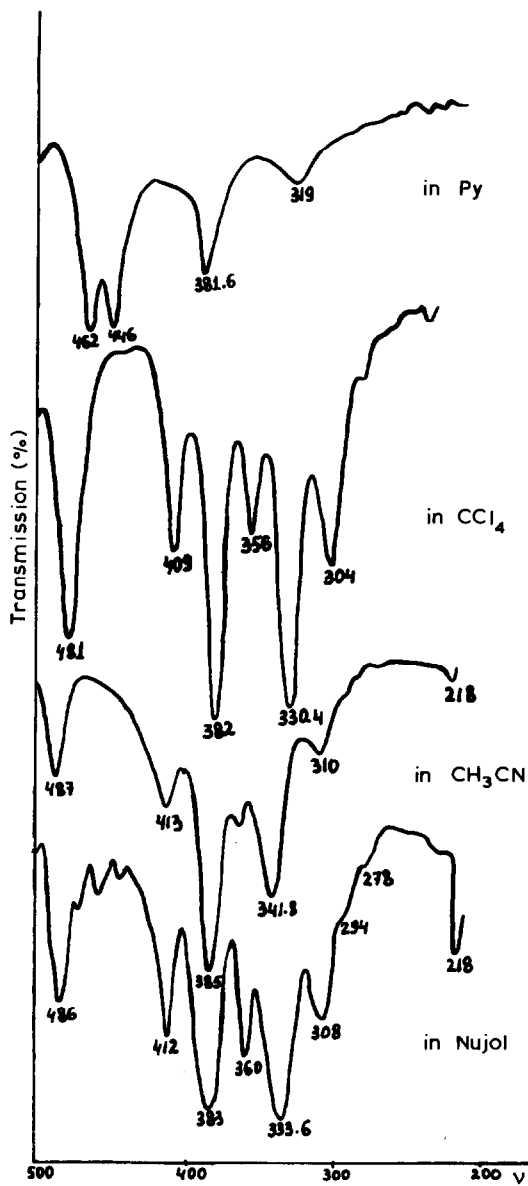
Fig. 2. IR spectra of 4-F-$C_6H_4COOCH_2SiF_3$ in the 500–200 cm$^{-1}$ region.

The 330 cm$^{-1}$ band for I in Nujol that we previously assigned to $\nu(O \rightarrow Si)$ is also in a satisfactory linear correlation with $\sigma_n$ of the substituent X (Fig. 4). Table 1 shows the O $\rightarrow$ Si frequency changing from 277 to 353 cm$^{-1}$ depending on the substituent X and the $\epsilon$ value of the medium. In this low-frequency region of the IR spectra of AFS there are more bands, in particular, 360, 218 cm$^{-1}$ (for I in the solid state), which we consider to be due to $\nu(O \rightarrow Si)$, though detailed analysis is impeded by their low intensity.

The behaviour of the $\nu(O \rightarrow Si)$ band in the spectra of AFS-pyridine complexes provides more evidence in favour of the band assignment. The spectra of solutions
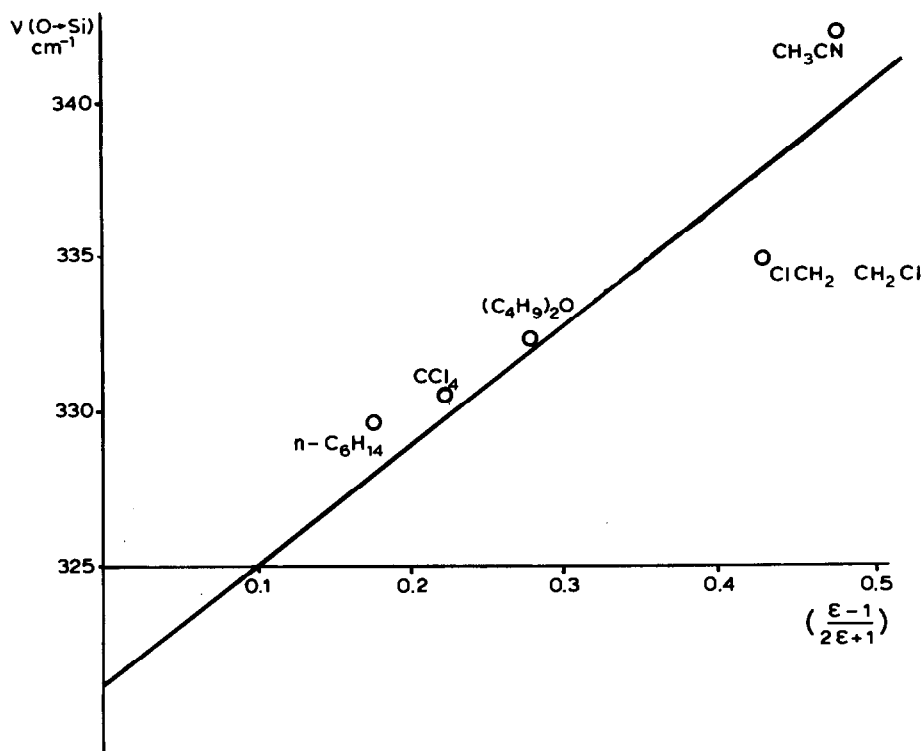
Fig. 3. Dependence of $\nu(O \rightarrow Si)$ on medium in the IR spectra of 4-F-$C_6H_4COOCH_2SiF$.

of I in $C_5H_5N$ and $C_5D_5N$ contain the $\nu(C=O)$ and $\nu(C-O-C)$ bands (1707 and 1320 $cm^{-1}$, respectively) characteristic of the non-coordinate carboxyl group, the $\nu(Si-F)$ bands being displaced to a lower-frequency region compared with the spectra of a pentacoordinate silicon. There are a number of bands (851, 769, 757, 740, 715, 689 $cm^{-1}$ with the major peak at 740 $cm^{-1}$) characteristic of a hexacoordinate silicon. This indicates breakage of the intramolecular $O \rightarrow Si$ bond and the formation of an intermolecular AFS-pyridine complex with $N \rightarrow Si \rightarrow N$ bonds. In the spectra of the $SiF_4 \cdot 2PhNH_2$ complexes the $\nu(Si-F_{hexa})$ bands occur at 800, 755, 735, 715, 695 $cm^{-1}$. The $\nu(Si-F)$ was to be expected at $\sim 380$ $cm^{-1}$ since the $\nu(N \rightarrow Si)$ for the $SiF_4 \cdot 2PhNH_2$ complexes occurs at 380–370 $cm^{-1}$ [7]. Unlike the spectra of solutions of I in various organic solvents, the spectra of I in $C_5H_5N$ contain no low-frequency bands that obviously correspond to $\nu(O \rightarrow Si)$. The most intense band at 338 $cm^{-1}$ disappears as well. At the same time, one can observe in this spectrum a new intense band at $\sim 380$ $cm^{-1}$, which may be assigned to $\nu(N \rightarrow Si)$, and bands at 464 and 485 $cm^{-1}$ which have evidently arisen from the $\delta(Si-F_{hexa})$ deformational vibrations. So, for the hexacoordinate complexes $SiF_4 \cdot 2Py$ the $\delta(Si-F)$ values are 490, 463 $cm^{-1}$.

Thus, all the data indicate that the band in the 330 $cm^{-1}$ region in the IR spectra of AFS is related to a greater extent to the $\nu(O \rightarrow Si)$ stretching vibration. For a theoretical substantiation of this suggestion we have carried out an analysis of normal vibrations of AFS molecules.
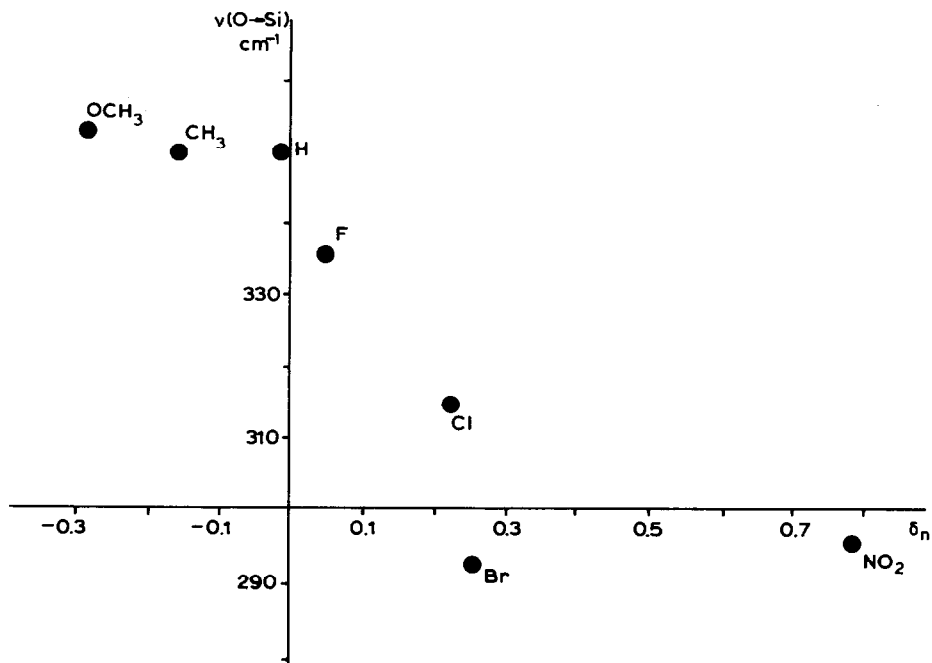
Fig. 4. Dependence of $\nu(O \rightarrow Si)$ on $\sigma_n$ of the substituent X in the IR spectra of AFS 4-X-$C_6H_4COOOCH_2SiF_3$.

## Calculations of the vibrational spectra of (=O → Si)-(aroyloxymethyl)trifluorosilanes

Vibrational calculations of pentacoordinate silicon compounds are scarce. They are only concerned with silatranes and $SiF_4 \cdot Py$ and $SiF_4 \cdot N(CH_3)_3$ complexes [8,9].

Table 1

$\nu(O \rightarrow Si)$ Frequencies $(cm^{-1})$ in the IR spectra of AFS 4-X-$CH_6H_4COOCH_2SiF_3$ upon varying the medium, $\epsilon$

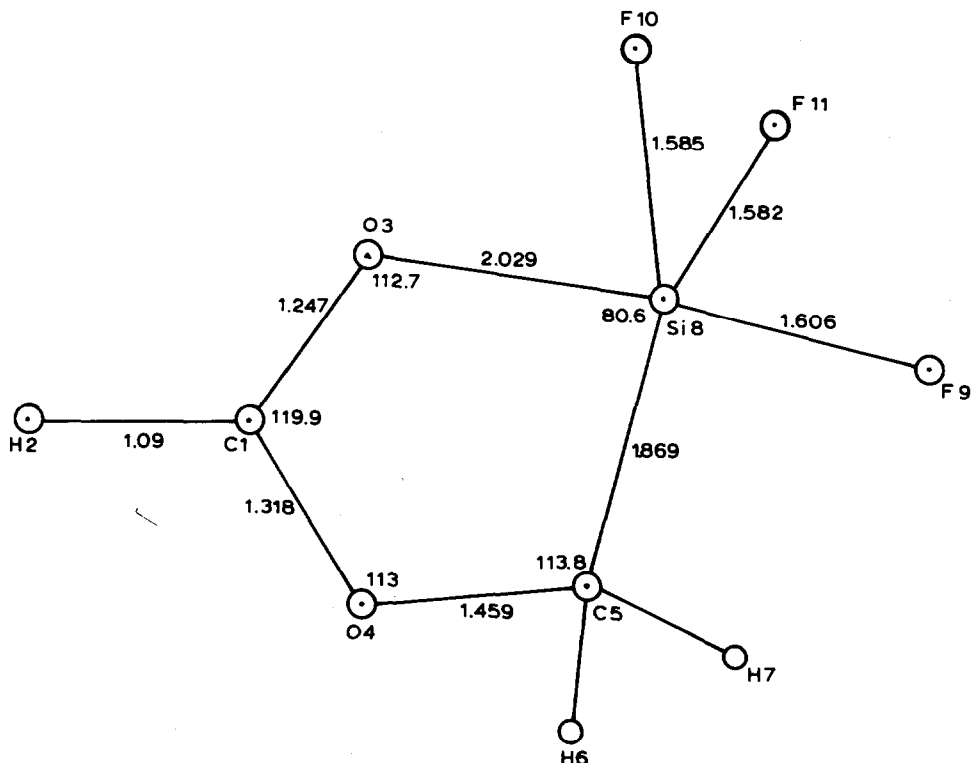| X | Medium, $\epsilon$ (25°C) | | | | | |
|---|---|---|---|---|---|---|
| | Nujol | $CH_3CN$ | $ClCH_2-CH_2Cl$ | $(C_4H_9)_2O$ | $CCl_4$ | $n-C_7H_{16}$ |
| | – | 0.48 | 0.43 | 0.29 | 0.225 | 0.19 |
| $CH_3O$ | 353 | 349 | – | 330 | – | – |
| | | | | 340 | | |
| $CH_3$ | 348 | – | 342 | 333 | 331 | 330 |
| H | 360 | – | – | 357 | 356 | 354 |
| | 349 | | | 337 | 338 | 337 |
| | 325 | | | 322 | 322 | 321 |
| F | 334 | 342 | 334 | 331 | 330 | 330 |
| Cl | 310 | – | – | 314 | 313 | 311 |
| Br | 287 | – | – | 283 | 279 | 277 |
| | | | | 277 | | |
| | | | | 269 | | |
| $NO_2$ | 296 | – | – | 294 | 293 | – |

Fig. 5. Model for calculating the $HCOOCH_2SiF_3$ normal vibrationy.

We attempted an evaluation of the force constant of bonds and angles of the silicon trigonal-bipyramidal envelope in AFS molecules and of the force constant of intramolecular coordinate interaction and its effect on other frequencies of the vibrational spectrum of these compounds. We rejected direct calculation from the experimental results, since aromatic substituents in molecules of type X-$C_6H_4COOCH_2SiF_3$ greatly complicate the analysis. The $H-COOCH_2SiF_3$ molecule was used as a model for calculating normal vibrations in a harmonic approximation (Fig. 5). The equilibrium geometry of the five-membered heterocycle corresponds to the experimental geometry of $4$-$F$-$C_6H_4COOCH_2SiF_3$ (I) in the crystalline state, deduced from X-ray diffraction [1].

The set of experimental frequencies, excluding the bands arising from the $4$-$F$-$C_6H_4$ group, also corresponds to the IR spectrum of crystalline I. The $4$-$F$-$C_6H_4$ group frequencies were excluded by comparison with the spectra of $CH_3COOCH_2SiF_3$ and of AFS with different substituents (X = $OCH_3$, $CH_3$, H, F, Cl, Br, $NO_2$). A tentative assignment of IR bands was made by analysis of the IR spectra of AFS in different media and by comparison with the spectra of the corresponding tetracoordinate silicon compounds $4$-$X$-$C_6H_4COOCH_2Si(OAlk)_3$. Non-planar coordinates were not introduced into the calculation because, due to their orthogonality with respect to planar coordinates, the interaction between the frequencies of non-planar and planar vibrations is negligible. The starting force field was taken block by block from calculations of the vibrational spectra of

CH$_3$C(O)OCH$_3$ [10], (CH$_3$)$_3$SiF [11], PF$_5$ [12] and pentacoordinate silicon complexes SiF$_4 \cdot$ N(CH$_3$)$_3$ [9]. A set of partial derivatives of frequencies by force constants permitted a force field corresponding to all the experimental frequencies for I in the crystalline state to be selected. Force constants in $10^6$ cm$^{-2}$ are given below. Bonds were numbered thus:
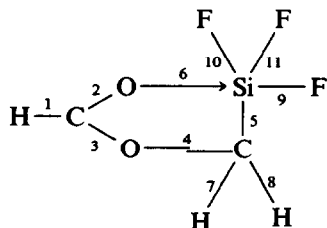


$K_1 = 8.0$, $K_2 = 18.1$, $K_3 = 13.1$, $K_4 = 8.1$, $K_5 = 5.3$, $K_6 = 0.96$, $K_7 = K_8 = 7.6$, $K_9 = 6.9$, $K_{10} = K_{11} = 7.9$, $K_{23} = 2.1$, $K_{34} = 3.2$, $K_{45} = 0.7$, $K_{56} = 1.1$, $K_{26} = 0.2$, $K_{78} = 0.75$, $K_{57} = K_{58} = 0.95$, $K_{47} = K_{48} = 0.7$, $K_{59} = 1.4$, $K_{5,10} = K_{5,11} = 2.0$, $K_{6,10} = K_{6,11} = 0.9$, $K_{69} = 1.2$, $K_{9,10} = K_{9,11} = 1.4$, $K_{10,11} = 2.0$, $H_{23} = 1.1$, $H_{26} = 0.2$, $H_{34} = 0.8$, $H_{56} = 0.1$, $H_{59} = 0.1$, $H_{5,10} = H_{5,11} = 0.3$, $H_{69} = H_{6,10} = H_{6,11} = 0.1$, $H_{10,11} = 1.2$, $H_{9,10} = H_{9,11} = 1.1$, $A_{23}^2 = 0.1$, $A_{34}^3 = 0.3$, $A_{34}^4 = 1.1$, $A_{45}^5 = 0.1$, $A_{56}^5 = A_{57}^5 = 0.1$, $A_{59}^5 = 0.1$, $A_{59}^9 = A_{5,10}^{10} = A_{6,10}^{10} = A_{10,11}^{10} = 0.3$, $L_{56}^{26} = L_{56}^{59} = 0.2$, $L_{56}^{5,10} = L_{56}^{5,11} = L_{59}^{5,10} = L_{59}^{5,11} = L_{59}^{69} = 0.2$.

Notes:     $K_i$ is the diagonal force constant of the $i$-th bond;

           $K_{ij}$ is the diagonal force constant of the angle formed by the $i$-th and $j$-th bonds;

           $H_{ij}$ stands for the non-diagonal force constant of the $i$-th and $j$-th bond interaction;

           $A_i^{jk}$ is the non-diagonal force constant of the interaction of the $i$-th bond and the angle between the $j$-th and $k$-th bonds;

           $L_{ij}^{kl}$ denotes the non-diagonal force constant of the interaction angles between the $i$-th and $j$-th bonds and $k$-th and $l$-th bonds, respectively.

The $K_{Si-F_{ax}}/K_{Si-F_{eq}}$ ratio $= 0.87$ is close to the force constant ratio for the axial and equatorial Si–F bonds ($\sim 0.76$) of the SiF$_4 \cdot$ N(CH$_3$)$_3$ complex [9]. The $K_{Si-F}$ values are lower than those of the tetracoordinate silicon ($\sim 9 \ 10^6$ cm$^{-2}$) in (CH$_3$)$_3$SiF [11]. The $K_{O \to Si}$ value of 0.96 is considerably smaller than the $K_{N \to Si}$ of 2.7 in silatranes [6], which correspond, to some extent, to the coordinate O $\to$ Si bond being weaker in AFS. In Table 2 the calculated and experimental stretching frequencies for I as well as their distribution of potential energy over vibrational coordinates are presented. The $\nu$(C=O) vibration is localized to the extent of 65% on the C=O bond, a percentage which remains practically unchanged over a wide range of force fields and with further variation of equilibrium geometry, corresponding to the change in the bond length, $l_{O \to Si}$. In principle this simulates AFS with different coordination strength (with different X and in media of different polarity and polarizability).

The SiF$_3$ group vibrations in the trigonal bipyramid are split into three vibrations, of which two (945 and 863 cm$^{-1}$) are mainly localized on the Si–F$_{eq}$ bonds, the 795 cm$^{-1}$ vibration being 79% localized on the Si–F$_{ax}$ bond.

Table 2

The observed and calculated frequencies and the potential energy distribution (PED) in the HCOOCH$_2$SiF$_3$ molecule

| $\nu_{exp}$ (cm$^{-1}$) $^{a,b}$ IR spectrum crystalline | $\nu_{calc}$ (cm$^{-1}$) | PED (%) $^c$ |
|---|---|---|
| 2915vw | 2913 | 50 CH$_6$, 50 CH$_7$ |
| 2846w | 2862 | 49 CH$_6$, 49 CH$_7$ |
| 1641vs | 1642 | 65 C=O, 9 C$_1$O$_4$, 13 C$_1$HO$_4$ |
| 1447m | 1451 | 19 CH$_6$, 19 CH$_7$, 46 CH$_6$H$_7$ |
| 1416s | 1422 | 7 C$_1$O$_4$, 25 O$_4$C$_5$, 12 CH$_7$O, 23 CH$_6$H$_7$ |
| 1366vs | 1357 | 6 C=O, 62 C$_1$O$_4$, 6 CH$_6$O, 6 CH$_7$O |
| 1160m | 1173 | 32 CH$_6$Si, 32 CH$_7$Si, 17 CH$_6$O, 17 CH$_7$O |
| 1011m | 1030 | 12 C$_1$HO$_3$, 15 COO, 28 OCC |
| 945vs | 958 | 12 CSi, 11 SiF$_9$, 22 SiF$_{10}$, 23 SiF$_{11}$ |
| 932s | 935 | 62 O$_4$C$_5$, 7 C$_1$HO$_4$ |
| 863s | 877 | 38 SiF$_{10}$, 36 SiF$_{11}$, 6 CH$_6$O, 6 CH$_7$O |
| 795s | 790 | 79 SiF$_9$ |
| 775m | 749 | 10 SiF$_{10}$, 10 SiF$_{11}$, 15 CH$_6$Si, 15 CH$_7$Si, 23 CH$_6$O, 23 CH$_7$O |
| 695w | 696 | 43 CSi, 18 SiF$_{10}$, 18 SiF$_{11}$ |
| 486w | 498 | 10 SiF$_{10}$C, 10 SiF$_{11}$C, 26 SiF$_{10}$F$_{11}$ |
| 383s | 380 | 38 SiF$_{10}$C, 37 SiF$_{11}$C |
| 360w | 361 | 16 Si O 15 SiF$_9$F$_{10}$, 19 SiF$_9$F$_{11}$, 20 SiF$_{10}$F$_{11}$ |
| 334vs | 331 | 23 SiO, 8 CSi, 16 COO, 8 SiF$_9$, 20 SiF$_{10}$F$_{11}$ |
| 308w | 299 | 43 SiF$_9$F$_{10}$, 37 SiF$_9$F$_{11}$ |
| 294vw | 296 | 8 CSi, 49 SiF$_9$C, 14 SiOF$_9$ |
| 218w | 224 | 34 SiO, 7 COSi, 11 SiOF$_{10}$, 16 SiOF$_{11}$, 8 SiOF$_9$, 16 SiF$_9$F$_{10}$ |
| — | 157 | 46 SiOF$_{10}$, 42 SiOF$_{11}$ |

$^a$ w = weak, vw = very weak, s = strong, vs = very strong, m = moderate. $^b$ Vibrational coordinates which contribute less than 6% are not taken into consideration. $^c$ Indices at the atoms in the PED column correspond to their numbering in Fig. 5.

The strong decrease in $\nu$(C=O) and $\nu$(Si–F$_{ax}$) frequencies with increasing strength of the coordinate bond (as seen from an experimental study of AFS and methyl(aroyloxymethyl)fluorosilanes) could be caused both by purely electronic effects (change in the force field of the molecule) and by kinematic effects (due to a change in equilibrium geometry). Analysis of the dependence of the calculated $\nu$(C=O) and $\nu$(Si–F$_{ax}$) frequencies on the force field mode indicates that the $K_{O \to Si}$ force constant does not greatly affect $\nu$(C=O) and $\nu$(Si–F$_{ax}$), whereas the non-diagonal force constants of the interaction of C=O and Si–F$_{ax}$ bonds with the O $\to$ Si bond and the angles at the silicon atom do influence them strongly. Thus, partial derivatives

$$\frac{\delta\nu(\text{C=O})}{\delta K_{O \to Si}} = 2 \text{ cm,}$$

$$\frac{\delta\nu(\text{Si–F}_{ax})}{\delta K_{O \to Si}} = 8 \text{ cm.}$$
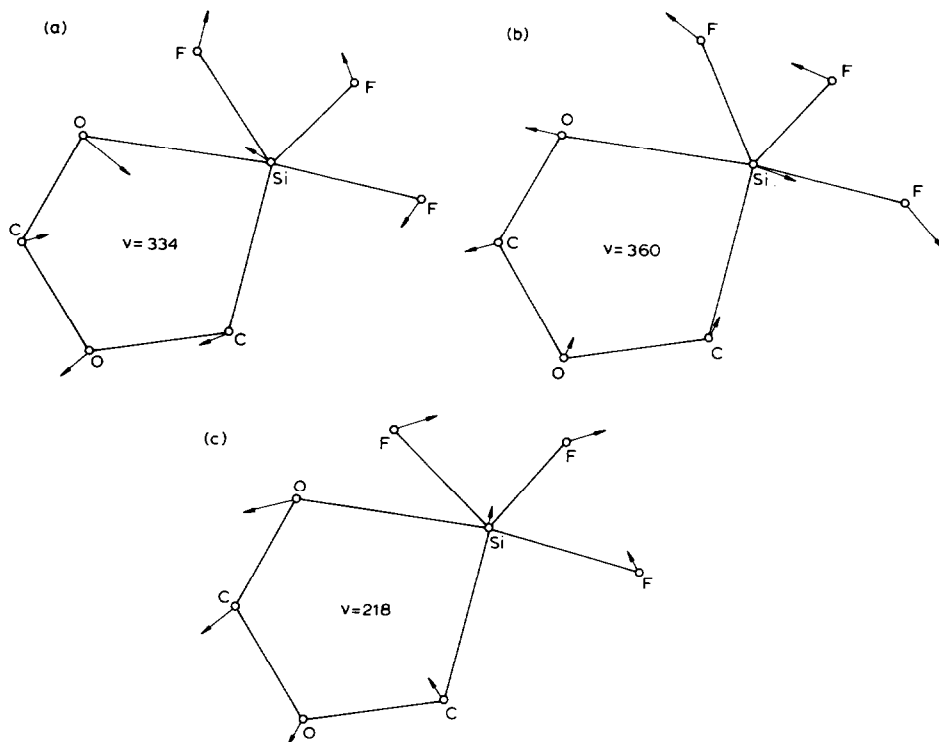
Fig. 6. (a, b and c) $\nu(O \rightarrow Si)$ vibrational modes in cartesian coordinates.

At the same time the partial derivatives of $\nu(C=O)$ and $\nu(Si-F_{ax})$ by non-diagonal force constants

$$\frac{\delta\nu(C=O)}{\delta K_{C=O,O \rightarrow Si}} \text{ and } \frac{\delta\nu(Si-F_{ax})}{\delta K_{Si-F_{ax},O \rightarrow Si}},$$

are $-15$ and $-41$ cm respectively.

The frequencies lower than 695 cm$^{-1}$ correspond mainly to vibrations due to stretching and deformational motions at the silicon atom (Table 2). Thus, the 486 cm$^{-1}$ vibration is related to the Si-F$_{eq}$-F$_{eq}$ angle. The vibrations at 383, 308 and 294 cm$^{-1}$ are associated with the Si-F$_{eq}$-C and Si-F$_{eq}$-F$_{ax}$ angle deformations. The frequency values of $\delta(Si-F)$ deformational vibrations are typical of those for pentacoordinate silicon compounds [7].

As expected, the O $\rightarrow$ Si stretching vibration is not strictly localized. It is spread over three low-frequency motions, 360, 334 and 218 cm$^{-1}$ (Table 2), which can be denoted as $\nu(\overset{1}{O} \rightarrow Si)$, $\nu\overset{2}{O} \rightarrow Si)$ and $\nu\overset{3}{O} \rightarrow Si)$, respectively. The vibrational modes involving the O $\rightarrow$ Si bond are shown in cartesian coordinates in Fig. 6.

The band at 330 cm$^{-1}$ in the IR spectra of AFS assigned to O $\rightarrow$ Si may correspond to both the 360 and 334 cm$^{-1}$ calculated frequencies.

The ranges of the O $\rightarrow$ Si force constant were evaluated for AFS in various media by consideration of the partial derivative
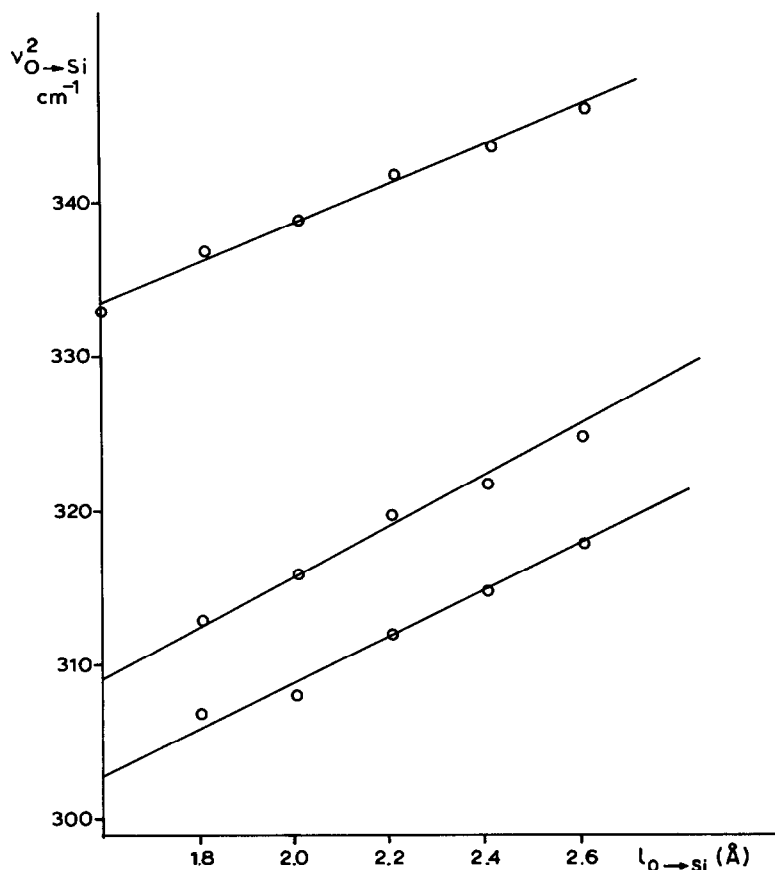
$$\frac{\delta\nu(O \rightarrow Si)}{\delta K_{O \rightarrow Si}}$$

Fig. 7. Dependence of $\nu_{O \to Si}^2$ on $l_{O \to Si}$.

in the range 40-80 cm for different sets of force fields. The $\nu(O \to Si)$ values for AFS range form 277 to 353 cm$^{-1}$ (Table 1). Thus, $K_{O \to Si}$ is from 0.2 to 1.2 $10^6$ cm$^{-2}$. For I the $\nu_{O \to Si}^{gas}$ value is 321 cm$^{-1}$ (from the correlation equation $\nu(O \to Si)$ $= f((\epsilon - 1)/(2\epsilon + 1))$ with $\epsilon = 1$). The force constant value for I in the gaseous state, $K_{O \to Si}^{gas}$ is from 0.6 to 0.8 $10^6$ cm$^{-2}$.

The change in the normal vibration frequencies in the spectra of AFS in response to varying strength of the intramolecular coordinate O → Si bond may be caused not only by electronic but also by kinematic factors. We have therefore calculated vibrations with the force field constant, but with varying equilibrium geometry. Tentative MNDO quantum-chemical calculations have been made of the model compound $HCOOCH_2SiF_3$ to study the effect of varying its geometry. The O → Si bond length changed from 1.6 to 2.6 Å, the molecular geometry being optimized by the full energy minimum for each $l_{O \to Si}$ value. The optimized geometry parameters thus obtained were used as equilibrium values in vibration calculations. Some sets of vibrational frequencies were calculated taking into account their dependence upon $l_{O \to Si}$. The 330 and 224 cm$^{-1}$ vibrations for I in the crystalline state are denoted as $\nu_{O \to Si}^2$ and $\nu_{O \to Si}^3$. The dependence of $\nu(C=O)$ and $\nu(O \to Si)$ $l_{O \to Si}$ are shown in Figs. 7–9. The $u''$ curves correspond to the force field selected for the molecule I.

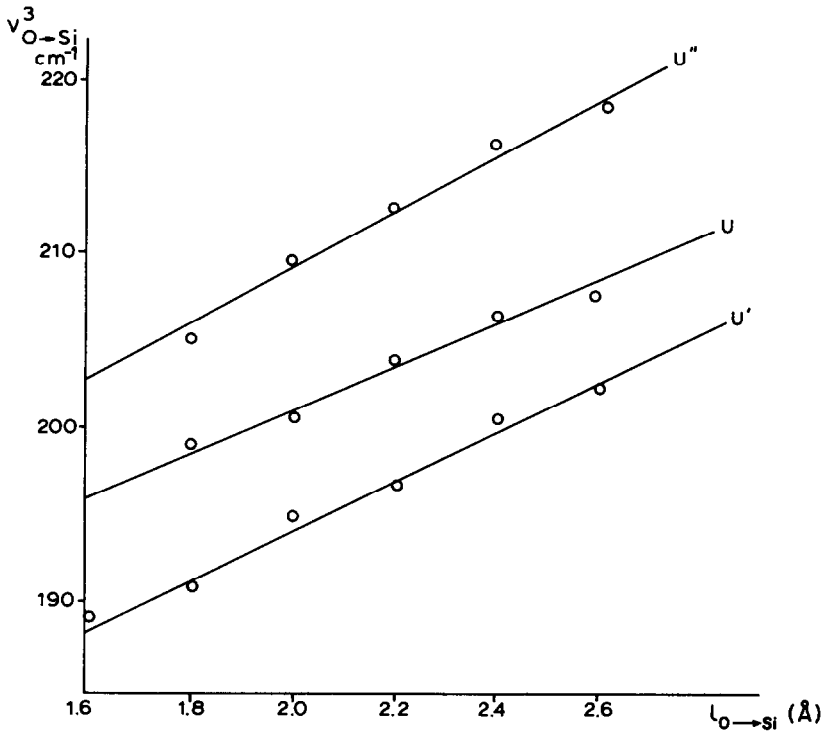Fig. 8. Dependence of $\nu_{O \to Si}^3$ on $l_{O \to Si}$.



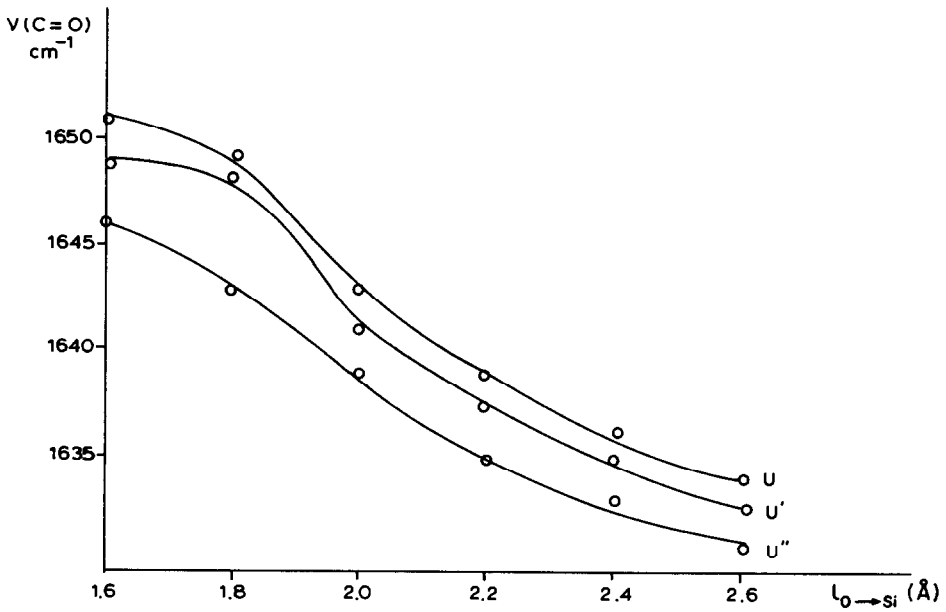Fig. 9. Dependence of $\nu(C{=}O)$ on $l_{O \to Si}$.

The $u$ and $u'$ curves correspond to defined force fields. The $\nu(C{=}O)$ and $\nu(O \rightarrow Si)$ frequencies increase in step with $l_{O \rightarrow Si}$. The changes in $\nu(C{=}O)$ and $\nu(O \rightarrow Si)$ with increasing $l_{O \rightarrow Si}$ are opposite to those observed experimentally. In fact, an increase in $\nu(C{=}O)$ and a decrease in $\nu(O \rightarrow Si)$ are observed with increasing coordinate $O \rightarrow Si$ bond length [4,5], i.e., with weakening donor-acceptor interaction. It is evident that purely kinematic factors may be responsible for a 15 cm$^{-1}$ decrease in $\nu(C{=}O)$, and a 10–20 cm$^{-1}$ increase in $\nu(O \rightarrow Si)$ when $l_{O \rightarrow Si}$ increases from 1.6 to 2.6 Å. This suggests that in AFS molecules change of vibrational frequencies may have as a main cause the electronic results of coordinate interaction.

## References

1 M.G. Voronkov and L.I. Gubanova, Main Group Met. Chem., 10 (1987) 209.

2 M.G. Voronkov, V.A. Pestunovich and Yu.L. Frolov, Advances in Organometallic Chemistry, MIR Publishers, Moscow, 1985, p. 54.

3 Yu.L. Frolov and M.G. Voronkov, J. Mol. Struct., 215 (1990) 265.

4 G.A. Gavrilova, N.N. Chipanina, Yu.L. Frolov, L.I. Gubanova, V.M. Dyakov and M.G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2251.

5 G.A. Gavrilova, N.N. Chipanina, Yu.L. Frolov, L.I. Gubanova, V.M. Dyakov and M.G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 1530.

6 I.S. Ignatyev, A.N. Lazarev, S.G. Shevchenko and V.P. Baryshok, Iz. Akad. Nauk SSSR, Ser. Khim., (1986) 1518.

7 A.A. Ennan, V.O. Gelmboldt and L.A. Gavrilova, Itogi nauki i tekhniki, Ser. Neorg. Khim., M., 15 (1989) 48.

8 I.R. Beattie, T.R. Gilson and G.A. Ozin, J. Chem. Soc. (A), (1986) 2772.

9 I.R. Beattie and G.A. Ozin, J. Chem. Soc. (A), (1970) 370.

10 Ye.M. Popov, G.A. Kogan, M.I. Struchkova and V.N. Zheltova, J. Strukt. Khimii, 12 (1971) 61.

11 A.N. Lazarev, I.S. Ignatyev and T.F. Tenisheva, Kolebaniya prostykh molekul so svyazyami Si ← O (Vibrations of simple molecules with Si ← O bonds), Nauka Publishers, Moscow, 1980, p. 23.

12 R.A. Condrate and K. Nakamoto, Bull. Chem. Soc. Jpn., 39 (1966) 1108.